Def Sci J, Vol 37, No 1, January 1987, pp 29–37.

ISRO Polyol – The Versatile Binder for Composite Solid Propellants for Launch Vehicles and Missiles

V.N. Krishnamurthy and Solomon Thomas

Vikram Sarabhai Space Centre, Trivandrum–695 022

ABSTRACT

A family of propellants based on a low cost hydroxy terminated binder has been developed and proved in large size motors. It can meet the requirements of Apogee motors as well as large boosters. The system offers advantages comparable with HTPB propellants in terms of high ballistic performance, stringent mechanical properties, ease and reliability of cure even at ambient conditions and high storage stability. The near-Newtonian flow behaviour, simplicity and processing characteristics of this saturated binder propellant are particularly note-worthy.

1. INTRODUCTION

The development of composite solid propellants in the last two decades the world over and particularly in India, has followed generally a pattern of continuing change dictated by requirements of higher ballistic performance coupled with better mechanical integrity under extreme operating conditions. The rocket propellant grain size has grown, in India, during this period, from RH 75 (75 mm dia.) weighing 4.5 kg to the 1st stage of the Polar Satellite Launch Vehicle (PSLV) weighing more than 125 tonnes. Correspondingly, the propellant technology also has moved from free standing to case-bonded grains for improving their performance. Keeping pace with this growth, the polymeric binder used in the propellants has undergone changes from the conventional polyvinyl chloride (PVC) to polybutadiene acrylic acid acrylonitrile terpolymer (PBAN), to carboxyl terminated polybutadiene (CTPB) and hydroxyl terminated polybutadiene (HTPB).

The propellants for launch vehicles are case bonded and have very high mass fraction (> 0.90) and high specific impulse. They have low modulus (<45 KSC) and high elongation. The propellants for sounding rockets and missiles are generally free

Received 25 August 1986

standing grains having a mass fraction of 0.50 - 0.90 in the vehicle. This calls for high modulus (>300 KSC) with high tensile strength combined with low elongation. In general, the conditions to which missile propellants are subjected during storage, transportation and flight are given in Table 1.

Table 1. Storage and transportation loads requirement for a missile propellant.

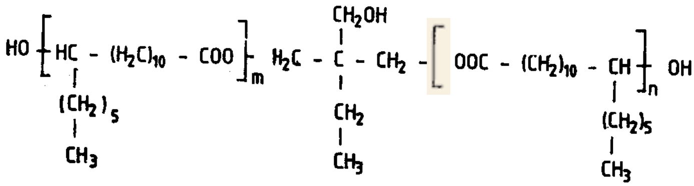
Temperature	-65°C to +70°C
Vibration	5 to 300 CPS
Shock	Upto 300 g
Acceleration	Upto 100 g
Spin rate	More than 200 RPS

The ballistic performance of the propellant is mainly governed by the solid loading which the polymeric binder can take up while the mechanical integrity is governed by the nature of the polymeric binder used. The solid composite propellants used, the world over, for these applications, are based on PBAN, CTPB or HTPB. ISRO has developed three more new polymeric binders, in addition to the above binders, for possible use in solid composite propellants. The High Energy Fuel 20 (HEF 20) is a substitute for CTPB[1] and has been used in the upper stages of Satellite Launch Vehicle-3 (SLV-3) and Augmented Satellite Launch Vehicle (ASLV) and as Apogee Kick Motor to put the 'Apple' satellite into orbit using Arian, ESA's launch vehicle. Another new propellant binder is ISRO polyol, a substitute for the HTPB binder. ISRO polyol based propellants are used in sounding rockets (RH 300) and was considered as a candidate propellant for the booster stages of Polar Satellite Launch Vehicle[2] (PSLV). The third new binder is hydroxyl terminated natural rubber (HTNR) and propellants based on this binder are under development[3].

The present paper enumerates the advantages of ISRO polyol as a binder which can meet the requirements of launch vehicles as well as missiles namely, high reliability and simplicity, the hall mark of solid propellants in addition to low cost.

2. NATURE OF POLYMERS

The ISRO polyol propellant binder based on castor oil is a saturated ester with a low molecular weight (~2000) nearly bifunctional prepolymer having a viscosity of about 2000 cp at 30°C. The hexyl-pendant groups impart good low temperature properties in addition to making it a self plasticized system. The chemical structure of the prepolymer can be represented as



This polyol is cured with isocyanates like toluene diisocyanate (TDI) or methylene diisocyanate (MDI). Trihydroxy compounds used as crosslinking agents e.g. castor oil, trimethylol propane (TMP) often serve to tailor the mechanical properties. The polymer can take different solid loadings and the effect of solid loading on the specific impulse is given in Fig 1. A family of propellants based on this polyol has been

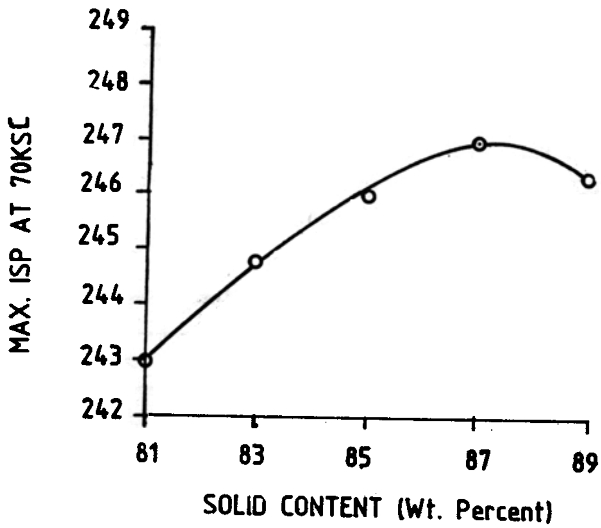


Figure 1. Expected specific impulse for the ISRO polyol propellant.

developed with a wide range of mechanical properties required for launch vehicles and sounding rockets/missiles. The salient properties are given in Table 2.

As the mechanical properties of the propellant depend on crosslinking agent, bonding agent and plasticizer level, in addition to the binder, the effect of these variables have been studied on the formulations designed for use in missiles[4] and launch vehicles.[5]

3. EFFECT OF CROSS-LINKING AGENT

As ISRO polyol functionality is slightly above 2, it needs a crosslinker to cure to rubbery mass with the isocyanate. Of the various trifunctional hydroxy compounds

Table 2. Physical and ballistic properties of the ISRO polyol based propellants.

Property	IPP–10	IPP–20	IPP–30	IPP–40	PEDPRO 1320
Solid loading (%)	83	83	84	87	87
Unloading viscosity (η) at 55°C (Poises)	8000	6400	8000	5000	10880
Specific gravity	1.74	1.74	1.79	1.8	1.81
Tensile strength (kg/cm^2)	5.5	6.2	29.7	5.8	5.6
Elongation (%)	45	75	16	35	32
Modulus (kg/cm^2)	37	32	210	35	38
Shore A hardness	68	70	78	72	67
Burning rate (mm/sec) at 70 kg/cm^2	6.2	6.2	8.5	6.1	10.8
Specific impulse (sec)	240	240	241	245	244

tried, such as castor oil, glycerol or trimethylol propane, the last named was found promising and hence used in the formulations. Keeping the solid loading at constant level, the cross-linker equivalents were varied and the mechanical properties studied. From the results given in Table 3, it is seen that tensile strength and initial modulus

Table 3. Effect of cross-linking agent (TMP) on the mechanical properties of ISRO polyol based propellant.

Solid loading (%)	Equivalents of cross-linking agent (%)	Mechanical properties T.S. (kg/cm^2)	E_b (%)	E_m (%)	E (kg/cm^2)
83	0	3.5	65	62	20
(unplasticised)	10	5.5	58	76	26
	20	7.2	50	87	34
84	0	3.7	58	55	14
(2% plasticised)	10	6.1	65	61	32
	20	10.7	45	41	58
	30	16.5	35	32	112
	40	22.1	27	25	150
	50	29.5	23	21	210
87	0	2.8	47	45	12
(1.5 % plasticised)	10	6.2	39	37	35
	20	10.5	30	28	60

of the propellant increases with the increasing concentration of the **cross-linker** while the elongation decreases indicating an increase in **cross-link** density with the increase in the trifunctional **cross-linker**

The isocyanate curing agent used in all the experiments is the 80 : 20 mixture of 2, 4 and 2, 6 isomers of toluene diisocyanate. As the strain capability of a propellant depends on the crosslink density of the binder matrix, the effect of the curing agent on the mechanical properties at a fixed **cross-linker** equivalent has been studied and the mechanical properties obtained are given in Table 4. Thus it is seen that the

Table 4. Effect of isocyanate equivalents on the mechanical properties of ISRO polyol based propellant.

Solid loading (%)	Equivalents of isocyanate curing agent (%)	Mechanical properties at 27°C			
		T.S. (kg/cm^2)	E_b (%)	E_m (%)	E (kg/cm^2)
84	90	18.0	25	22	120
	95	22.1	22	20	152
	98	27.6	20	17	184
	100	29.8	17	15	250
87	90		not	cured	
	95	3.9	43	41	28
	98	5.6	36	33	35
	100	7.2	25	22	50

mechanical capabilities of the polymer network could be exploited to the maximum extent at an *NCO/OH* ratio nearest to unity. The inherent nature of the *OH* groups due to their position in the molecule facilitated long pot-life.

4. EFFECT OF OXIDIZER BONDING AGENTS

Improvements in the bonding characteristics of oxidizer and binder enhances the mechanical properties of the system. In polyurethane propellants, bonding agents play a very important role in the mechanical properties so that they have become almost a must in propellant composition.[6] An alkanolamide type (POB), aziridine type (MT), and neutral compound type (TMP) were tried and their effect on the propellant properties and processability are given in Table 5 and Fig. 2 respectively. The low molecular weight and higher polarity facilitates TMP to attach itself all over the ammonium perchlorate particles easily and form a tough shell,on the addition of toluene diisocyanate thereby shifting the void formation site away into the matrix phase.

Table 5. Effect of oxidizer bonding agent equivalent on the mechanical properties of the solid propellants.

Solid loading (%)		Equivalents of bonding agent (%)	Mechanical properties at 27°C T.S. (kg/cm^2)	E_b (%)	E_m (%)	E (kg/cm^2)
83		0	3.5	58	55	14
	MT	4	5.8	64	61	28
		8	7.2	48	45	37
		12	7.9	43	40	46
		16	8.6	36	32	58
	POB	4	6.8	37	35	39
			6.5	45	42	34
		12	7.4	43	41	38
		16	7.8	35	32	49
	TMP	10	4.0	74	71	20
		15	6.2	48	45	39
87	TMP	0	2.8	25	22	18
		5	3.4	28	26	16
		10	4.3	32	30	18
		15	6.0	41	39	28
		20	6.5	30	28	41

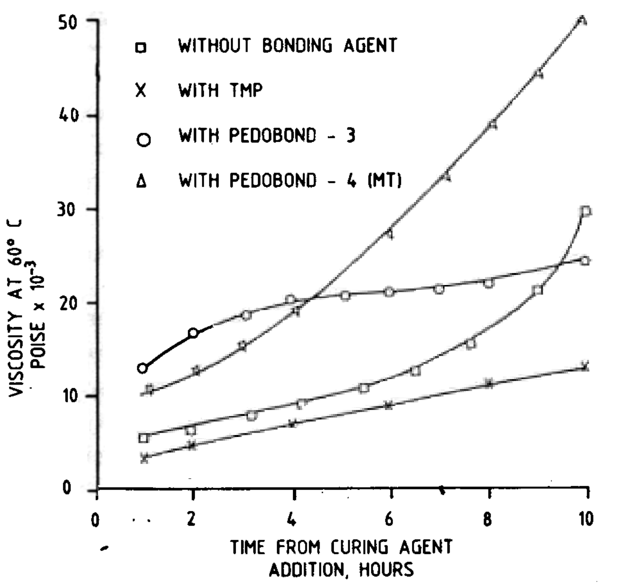
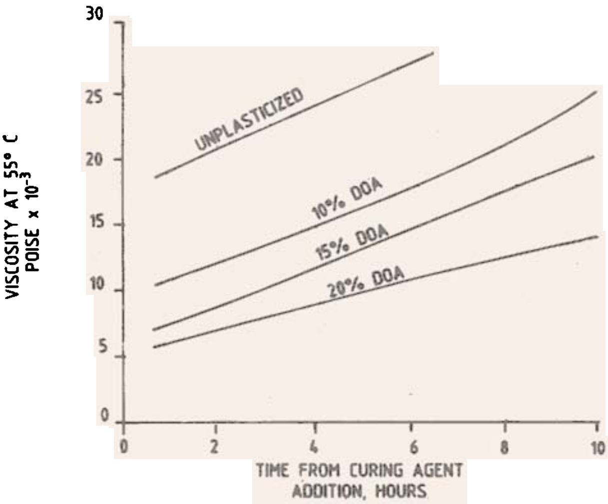


Figure 2. Effect of bonding agent type on viscosity of ISRO polyol propellant.

The processability of the propellants in presence of the bonding agents as shown by the unloading viscosity and its build up with time indicates that TMP is a better bonding agent compared to the other two.

5. EFFECT OF PLASTICIZER

The C_6 pendant chain makes ISRO polyol a self plasticized system. Thus, the polyol at 83 per cent solid loading has good processability and mechanical properties. Since these propellants contain no additional plasticizer, the problem of plasticizer migration from propellant to insulation does not arise. In order to increase the solid loading and flexibility, various plasticizers have been incorporated in the formulations. Dioctyl adipate (DOA) was chosen as the material for further processing because of cost and availability considerations. The viscosity build up, when DOA is used is given in Fig. 3. The effect of DOA level on the mechanical properties of the propellant is given in Table 6. It is found that increasing the plasticizer content leads to decrease in the mechanical properties.



Effect of plasticizer level on the viscosity of 87% loaded IPP 40 ISRO polyol proprllant.

Table 6. Effect of DOA level on the mechanical properties of 87% loaded ISRO polyol propellant.

DOA level of binder (%)	Mechanical properties at 27°C			
	T.S. (kg/cm²)	E_b (%)	E_m (%)	E (kg/cm²)
10				
15				
20				

6. AGEING STUDIES

Apart from its dependence on the composition, the mechanical properties also vary with temperature. Table 7 gives the properties of the two compositions at the chosen temperatures.

Table 7. Low temperature properties of the ISRO polyol propellants.

Solid loading (%)	Temperature (°C)	Mechanical properties T.S. (kg/cm^2)	E_b (%)	E (kg/cm^2)
84	27	25.8	18	200
	0	32.6	20	280
	−20	37.3	18	350
87	27	7.3	40	45
	0	9.0	46	50
	−15	17.3	36	112
	−30	36.0	28	210

The mechanical properties of a propellant can vary on storage due to ageing. This variation in properties is important for missile applications as the grains are stored for long durations. The propellants deployed in missiles undergo thermal cycling because of the environmental temperature changes. To get an insight into this, the propellants were stored at extreme temperatures and their mechanical properties evaluated as a function of time. Using Arrhenius equation, the life at ambient temperature storage can be predicted. Based on the accelerated ageing studies given in Table 8, the life of the propellants based on ISRO polyol is estimated to be more

Table 8. Accelerated ageing studies on ISRO polyol based propellants.

Solid loading (%)	Time days	Mechanical properties T.S. (kg/cm^2)			E_b (%)		
		60°C	75°C	90°C	60°C	75°C	90°C
84	0	25.8	25.8	25.8	20.0	20.0	20.0
	50	26.1	26.0	26.2	20.0	19.0	18.0
	100	25.9	25.7	25.9	19.0	17.0	16.0
87	0	5.8	5.8	5.8	40.0	40.0	40.0
	50	5.8	5.8	5.9	40.0	40.0	38.0
	100	5.8	5.8	6.1	39.0	38.0	35.0

than eight years. This can be expected as ISRO polyol backbone has a saturated carbon chain compared to the conventional binders such as HTPB or CTPB which have double bonds susceptible to oxidative degradation in the chain.

Thermal cycling of the propellant samples have also been carried out to make sure that polymer is stable against thermal and oxidative degradation. Samples were kept at 135°C for 16/24 hours and cooled to ambient and again heated to 135°C and tested. The propellants withstood 6 cycles without any deterioration in mechanical properties. This also showed that the propellants were fit for heat sterilisation, if required.

7. CONCLUSION

The above studies indicate that ISRO polyol based propellants can be tailored to meet the requirements of a range of mechanical properties as required by the application viz., for missiles or launch vehicles and can still have good ageing characteristics.

The ballistic property requirements – burning rate and specific impulse – can be met with a judicious combination of oxidizer particle size, coarse and fine ratio, combined with catalysts at suitable solid loadings.

The easy availability and low cost makes ISRO polyols more attractive compared to current binders like PBAN, CTPB and HTPB.

REFERENCES

1. Rao, K.V.C., Sreedhar Jayadev, Varghese, T.L. & Gowariker, V.R., *J. Spacecraft*, **15** (1978), 293-298.

2. Nema, S.K., Francis, A.U., Nair, P.R. & Gowariker, V.R. Low oxygen containing polyesters in low cost polyurethane propellants for large booster applications , AIAA/SAE 15th Propulsion Conference, Palo Alto, California, 26-27 July, 1976.

3. Gupta, S.K., Kurup, M.R., Devdoss, E., Muthiah, R.M. & Solomon Thomas, *J. Applied Polymer Science*, **30** (1985), 1095-1112.

4. Solomon Thomas & Krishnamurthy, V.N., Development of a high tensile polyurethane propellant, Symposium on High Energy Materials, ERDL, Pune, 21-23 January,1982.

5. Krishnamurthy, V.N., Solomon Thomas & Janardhanan, M., Development of a versatile ISRO polyol propellant, Symposium on Chemical and Mechanical Technologies of Propellants and Explosives, Karlsrube, W. Germany, 1-3 July,1981.

6. Solomon Thomas, Nair, P.R. & Krishnamurthy, V.N., Experimental and mechanistic aspects of oxidizer bonding agents in solid propellants, Proceedings of DAE Symposium on Strengthening Mechanism in Solids Suratkal, Karnataka, 23-25 February, 1981, pp 127-138.